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HYDROGENATION OF ALKENES BY THE COMPLEX OF CROSS-LINKED POLYACRYLIC ACID WITH RHODIUM(111)

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The complex of cross-linked polyacrylic acid with rhodium(111) catalyzes the heterogeneous hydrogenation of terminal and internal alkenes in polar solvents at 30°C under an atmospheric hydrogen pressure. The C=C double bonds can be hydrogenated selectively by the complex catalyst for the hydrogenation of the alkenes with carbonyl and aromatic groups.

In the previous paper,[1)] the brownish-dark green complex of polyacrylic acid with rhodium(111) was found to catalyze the homogeneous hydrogenation of a number of alkenes in methanol solution at 30°C under an atmospheric hydrogen pressure. In this letter, we wish to report that a brownish-dark green polymer complex obtained under refluxing of cross-linked polyacrylic acid partly displaced with rhodium(111) ion is very active and highly selective toward the C=C double bonds for the hydrogenation of terminal and internal alkenes and alkenes with carbonyl and aromatic groups.

A carboxylic cation exchange resin based upon acrylic acid-divinylbenzene copolymer, Amberlite IRC-84 (Rohm and Haas) was used as a cross-linked polyacrylic acid ligand. A solution of $RhCl_3.3H_2O$ (1.0 or 0.1 mmol) in methanol (30 ml) was added to water (100 ml) contained Amberlite IRC-84 (Na) (17.0 ml, 35 meq. as carboxyl group) and the solution was stirred at 50°C for 5 hr. After decantation to remove a small amount of brown substance like alga formed during stirring, the bitter orange-colored resin particles partly displaced with rhodium(111) ion were collected by filtration, washed with water (100 ml), and refluxed in methanol(50 ml)-

water(50 ml) solution under nitrogen for ca. 8 hr to yield brownish-dark green particles of polymer-rhodium complex. The brownish-dark green particles of the IRC-84-Rh complex were collected by filtration, washed with methanol (100 ml), and stored in methanol. Hydrogenation of substrates under an atmospheric hydrogen pressure was carried out using the apparatus and the procedure described in the previous paper.1) A 200 ml stainless steel autoclave equipped with an inner glass cell and a rotation agitator was also used for hydrogenation of substrates under compressed hydrogen gas. The reaction products were analyzed by glpc with a 5 m column of diethylene glycol containing $AgNO_3$, a 2 m column of polyethylene glycol containing $AgNO_3$, or a 2 m column of polyethylene glycol 6000.

Under refluxing in pure water instead of in the methanol-water solution mentioned above, the bitter orange-colored resin particles became yellow particles which were scarcely active for the hydrogenation of hex-1-ene. On the other hand, under refluxing in pure methanol, the bitter orange-colored particles gave a small amount of fine black precipitate and became dark brown particles which were very active for the hydrogenation of hex-1-ene and also active for the hydrogenation of benzene. The high catalytic activity of the dark brown particles may be attributed to the rhodium metal reduced under refluxing. The brownish-dark green particles of the IRC-84-Rh complex obtained under refluxing in the methanol-water solution were as active as the dark brown particles for the hydrogenation of hex-1-ene, but not active for the hydrogenation of benzene. In the present study the catalytic behavior of the brownish-dark green particles of the IRC-84-Rh complex will be investigated in detail.

Some representative rates of initial hydrogen uptake for the hydrogenation of alkenes and alkynes at 30°C under an atmospheric hydrogen pressure are given in Table 1. The IRC-84-Rh complex is very active for the hydrogenation of straight chain terminal and internal alkenes, straight diene, and cyclic diene and monoene. The catalytic activities per rhodium atom2) of the IRC-84-Rh complex for the hydrogenation of hex-1-ene in ethanol and in dimethylformamide are more than 200 times and 20 times, respectively, as much as those of $Rh_2(OCOCH_3)_4$ complex.3)

Though the IRC-84-Rh complex functions as an excellent catalyst for the hydrogenation of alkenes, the complex catalyst is much less active for the hydrogenation of alkynes, as shown in Table 1. Addition of hex-1-yne (0.1 mol/l) into the catalytic system caused a marked decrease in the rate of hydrogenation of

Table 1. Rates of Hydrogenation of Substrates by Complex of Cross-Linked Polyacrylic Acid with Rh(111); catalyst, 4.0 ml in methanol, Rh≦0.05 mmol; substrate concentration, 0.4 mol/l; total volume of reaction mixture, 50 ml; temp., 30 ± 0.05°C; H_2 pressure = 76cmHg - vapour pressure of solvent media.

Solvent	Substrate	Initial hydrogen uptake in ml/min at s.t.p.
MeOH	Hex-1-ene	9.42
"	trans-Hex-2-ene	6.55
"	cis-Hex-2-ene	7.63
"	Dec-1-ene	7.50
"	Hexa-1,5-diene	6.89
"	α-Acetamidocinnamic acid	a)
"	α-Acetamidoacrylic acid	6.12 b)
"	Maleic acid	11.4
"	Itaconic acid	7.72
"	Dimethyl maleate	7.92
"	Dimethyl itaconate	8.40
"	Cycloocta-1,3-diene	10.1
"	Cyclooctene	5.92
"	Hex-1-yne	0.36
"	Hex-1-yne-3-ol	0.51
"	Mesityl oxide	5.22
$MeOH-H_2O$ c)	"	1.85
EtOH	Hex-1-ene	5.52 d)
$HCONMe_2$	"	2.47 e)
$MeCONMe_2$	"	2.43
Me_2SO	"	a)

a) No hydrogenation observed.

b) Temp., 35°C; substrate concentration, 0.17 mol/l.

c) Reaction mixture contains 20 ml H_2O.

d) 5.52 ml/min = 8.21×10^{-5}mol/l sec.

e) 2.47 ml/min = 3.67×10^{-5}mol/l sec.

alkenes.

Glpc analysis of the reaction mixture obtained for the hydrogenation of hex-1-ene in methanol indicated that n-hexane was produced accompanied with small amounts of isomerized alkenes; trans-hex-2-ene (about 20% in maximum value), cis-hex-2-ene (about 15% in maximum value), trans-hex-3-ene (about 3.0% in maximum value), and a trace of cis-hex-3-ene. These isomers were hydrogenated completely to hexane for further hydrogenation. In the case of dec-1-ene, trans- or cis-hex-2-ene as substrate, small amounts of isomerized alkenes were also found during hydrogenation. Under the reaction conditions used, no isomerization reaction was observed in the absence of hydrogen gas.

As shown in Table 1, the unsaturated acids such as itaconic acid and maleic acid are easily hydrogenated as well as their methylesters. The hydrogenation of α-acetamidoacrylic acid proceeded efficiently, whereas that of α-acetamidocinnamic acid was suppressed entirely, even at 50°C.

The catalytic activity of the IRC-84-Rh complex was found to depend strikingly on the sort of solvent media. As shown in Table 1, alcohols are the most profitable solvents for the catalytic activity of the IRC-84-Rh complex. For the hydrogenation of hex-1-ene in dimethyl sulfoxide, no hydrogenation was observed. Though the addition of small amounts of water (0-0.2 mol/l) to the reaction mixture does not cause any marked effect on the initial rate of hydrogen consumption, the rate decreases considerably when a large amount of water (about 40% in volume) is added to the methanol used as solvent, as shown in Table 1. The catalytic activity of the IRC-84-Rh complex dried at 50°C in vacuo for ca. 5 hr decreased to about one-third of that of the original one.

The IRC-84-Rh complex was not active for the hydrogenation of 1,2-epoxyoctane under the conditions of temperature and hydrogen pressure as given in Table 1. On the other hand, 45 ml of hydrogen gas was consumed for 60 min for the hydrogenation of 1,2-epoxyoctane (20 mmol) in methanol catalyzed by a commercial rhodium-active carbon catalyst (Japan Engelhard Co.)(Rh/C, 0.41 g, contains 0.2 mmol of Rh) under the same conditions and about 10% of octanol-2 was detected in the reaction mixture.

The hydrogenation of mesityl oxide and styrene was carried out under initial hydrogen pressure of 30 or 70 Kg/cm^2 at 30°C using the IRC-84-Rh complex and the Rh/C catalyst as a reference. The plots of hydrogen pressure in the autoclave against reaction time showed that the complex catalyst was slightly less active than the Rh/C catalyst for the hydrogenation of the C=C double bonds of the substrates and the hydrogenation of the C=C double bonds in the side chain of styrene or in mesityl oxide catalyzed by the complex catalyst was completed within about 25 min without any following hydrogen uptake. The reaction conditions and the results of the hydrogenation are summarized in Table 2.

It can be seen from Table 2 that the catalytic behaviors of the complex catalyst are quite different from those of the Rh/C catalyst which is active for the hydrogenation of carbonyl and aromatic groups. The IRC-84-Rh complex is scarcely active for the hydrogenation of such groups even under compressed hydrogen gas.

Preliminary kinetic study was carried out using hex-1-ene as substrate and the IRC-84-Rh complex as catalyst at 30°C under an atmospheric hydrogen pressure. The reaction was first order in the catalyst concentration and the dependence on the olefin concentration changed from first order to zero order as the olefin concentration increased.

Comparing the catalytic activity of the IRC-84-Rh complex with that of the

Table 2. Catalytic Hydrogenation of Mesityl Oxide and Styrene; substrate, 5.0 g; solvent, methanol 50 g; temp., 30°C; reaction time, 60 min; initial H_2 pressure, 30 Kg/cm^2.

Catalyst (Rh, mmol)	Substrate	Product	Yield(%)
IRC-84-Rh[a] ($\leqq 1.0$)	Mesityl oxide	Methylisobutylketone	100.0[b]
		4-Methylpentanol-2	trace
Rh/C[c] (0.5)	"	Methylisobutylketone	38.7
		4-Methylpentanol-2	61.3
IRC-84-Rh[a] ($\leqq 1.0$)	Styrene	Ethylbenzene	98.9
		Ethylcyclohexane	1.1
Rh/C[c] (0.5)	"	Ethylbenzene	38.3
		Ethylcyclohexane	61.7

a) Complex catalyst, 8.0 ml in methanol was used.

b) Initial H_2 pressure, 70 Kg/cm^2 was applied and reaction time, 100 min.

c) Rhodium content, 5% in weight.

homogeneous polyacrylic acid-rhodium complex described in the previous paper,1) the IRC-84-Rh complex is less active than the homogeneous catalyst for the hydrogenation of alkenes. The IRC-84-Rh complex hydrogenates itaconic acid as well as dimethyl itaconate in contrast with n-propylammonium salt of polyacrylic acid-rhodium complex which is much less active for the hydrogenation of itaconic acid than for that of its methylester.1) Other marked difference between the catalytic behaviors of the IRC-84-Rh complex and the homogeneous polymer complex is observed in that the former is much more active than the latter for the isomerization of alkenes during hydrogenation of them.1)

The particles of the IRC-84-Rh complex found to be rigid and to remain brownish-dark green throughout the course of reaction. The complex catalyst is quite stable and can be handled in the presence of oxygen without any marked decrease in catalytic activity. At the completion of hydrogenation of substrates, the particles of the polymer complex can be easily recovered and reused without any appreciable loss in activity.

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1) Y.Nakamura and H.Hirai, Chemistry Letters, 1974, in press.

2) The activity per rhodium atom was calculated using the charged amount of rhodium, 0.05 mmol: 4.0 ml of the particles of the IRC-84-Rh complex (17.5 meq. as carboxyl group) in methanol. In the preparation of the complex, about 10% of the charged rhodium was lost as the brown substance like alga. Consequently, the true value of the activity per rhodium atom may be larger than the calculated value.

3) According to the literature,4) the initial rates of hydrogen uptake using $Rh_2(OCOCH_3)_4$ catalyst were 0.51×10^{-5} mol/l sec in ethanol and 2.28×10^{-5} mol/l sec in dimethylformamide under the conditions:catalyst concentration, 5.0 mmol/l; hex-1-ene concentration, 1.0 mol/l; temp., 30°C; atmospheric hydrogen pressure.

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